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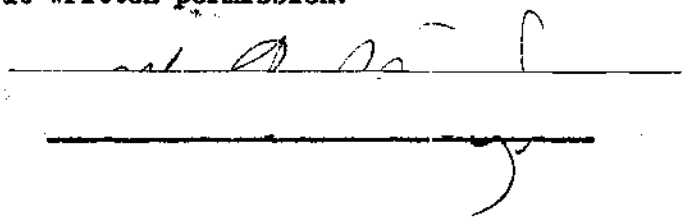

DESIGN OF A CONTINUOUS FLOW STIRRED TANK REACTOR TO DETERMINE THE KINETIC PROPERTIES OF A HOMOGENEOUS GAS PHASE REACTION

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SUMMARY

Two methods have been used almost exclusively for determination of rate constants of chemical reactions. These two methods are known as the batch method and the tubular flow method. In 1944 Denbigh proposed a third method to determine the reaction rate constants of chemical reactions which is known as the continuous flow stirred tank reactor method. A few articles, based on Denbigh's suggestion, have appeared in the literature which dealt with the use of the continuous flow stirred tank reactor method to determine the rates of reaction of homogeneous reactions in the liquid phase only. Studies of gas phase reaction rates have not appeared in the literature to date.

Since the use of the continuous flow stirred tank reactor method has been restricted to homogeneous liquid phase reactions, the purpose of this work was (1) to critically review all available literature which pertained to the use of the continuous flow stirred tank reactor method for the determination of reaction rate constants, (2) to determine the advantages and the disadvantages of the continuous flow stirred tank reactor method as compared to the tubular flow method and the batch method, (3) to consider theoretically the possibility of determining reaction rate constants of homogeneous gas phase reactions using the continuous flow stirred tank reactor method, and (4) to design a continuous flow stirred tank reactor system for the determination of the reaction rate constants of a specific homogeneous gas phase reaction.

The literature review revealed that the continuous flow stirred

tank reactor method has been used to determine accurately the rate constants of a variety of homogeneous liquid phase reactions. The reactions studied included simple second order reactions, very fast reactions, and complex reactions, i.e., reactions whose rates of reaction depend upon intermediate products formed during the reaction as well as the reactants and final products, or reactions whose reaction rates depend upon competing side reactions which occur simultaneously with the main reaction.

After careful consideration of all design factors the conclusion was reached that the continuous flow stirred tank reactor method is feasible for the determination of the rate constants for homogeneous gas phase reactions.

From reported experimental work as well as from a theoretical analysis of the continuous flow stirred tank reactor it was concluded that the primary advantage of using the continuous flow stirred tank reactor method to determine reaction rate constants for either gas or liquid phase reactions as compared with the tubular flow and the batch methods is the mathematical simplicity of rate constant equations. The simplicity of mathematical calculations necessary to calculate the reaction rate constants makes the continuous flow stirred tank method particularly useful in analyzing complex or simultaneous reactions by eliminating the difficult and time consuming task of solving the complex integral equations that result from the tubular flow and batch methods.

The continuous flow stirred tank reactor method has the unique advantage that a reaction can be studied at any stage of the reaction process because the rate change of the concentration of all the reaction

constituents is zero at steady state. However, the continuous flow stirred tank reactor method has the disadvantage of requiring, in most cases, a longer time to complete an experiment, i.e., determine one rate constant for one set of conditions, and the expenditure of more chemicals than either of the other two methods. It is shown that the time required for the completion of an experiment for most reactions when the continuous flow stirred tank reactor system is used can be held within reasonable operating limits by proper design of the system.

A design is presented of a continuous flow stirred tank reactor system which can be used to determine the rate constants of the gas phase reaction between methane and sulfur at a pressure of one atmosphere and temperatures between 550° C and 625° C. The resultant design provides a simple system of moderate construction cost and one whose operating expenses will be low because the small size requires a small expenditure of chemicals for each experiment.

CHAPTER I

INTRODUCTION

The design of equipment for carrying out chemical reactions has been largely empirical. However, considerable progress has been made in the past twenty years toward placing equipment design on a scientifically sound theoretical basis. The design problem can be divided into two parts: the first is concerned with reaction mechanism or kinetics and the second is concerned with using this kinetic information to design equipment which will give the desired results.

Over a period of many years two methods have been used almost exclusively for the determination of kinetic properties of systems undergoing chemical reaction. The first, and most generally used on a small scale in the laboratory, is referred to as the batch method. This method involves placing known amounts of reactants into the reactor vessel and allowing the reaction to proceed at constant temperature and pressure for a given length of time. The composition of the reaction mixture is then determined as a function of time and this data used to determine the reaction rate.

The second method utilizes a tubular flow reactor. The reactants are continuously introduced in one end of a long tube and the products are continuously removed from the other end. It is important in this type of reactor that there be essentially no mixing in the direction of flow as materials traverse the reactor tube.

A third method was suggested by Denbigh (1)* in 1944. This method makes use of a continuous flow reactor of the type commonly used in industry for production. However, prior to Denbigh's article, no mention has been made in the literature of its use for determining kinetic properties of reactions. With this method the reactants are introduced continuously into a tank reactor which is stirred and the products are removed continuously as in the tubular reactor. In contrast with the tubular reactor system the composition of the reaction mixture should be essentially constant throughout the tank reactor.

Very little experimental work has been done using the continuous flow stirred tank reactor to determine reaction rate and order. Denbigh (2) has published one paper. Hammett and co-workers (3), (4), (5), (6), (7) have published several other papers which follow Denbigh's method. All of the papers have dealt with homogeneous liquid phase reactions and none with gas phase reactions.

Since no study of gas phase reactions with the continuous flow stirred tank reactor method has been made, the objectives of this work are the following:

(1) To investigate theoretically the possibility of determining reaction rate constants for homogeneous gas phase reactions using a continuous flow stirred tank reactor (Denbigh's method).

(2) To determine the advantages and disadvantages of Denbigh's method for homogeneous gas phase reactions as compared with the two classical methods.

(3) To critically review all available literature which has a

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*Numbers in parentheses in the text refer to the bibliography.

bearing on Denbigh's method.

(4) To design a continuous flow stirred tank reactor for the determination of the reaction rate constants of a specific homogeneous gas phase reaction.

CHAPTER II

REVIEW OF WORK DONE

Denbigh (8) briefly compared theoretically the batch system, the continuous flow tubular system and the continuous flow stirred tank reactor; from this comparison he suggested that the continuous flow stirred tank reactor* theoretically offered advantages over the other two systems for determining reaction rates and order for liquid phase reaction.

To summarize his analysis for irreversible reaction, consider a batch reaction where:

$$hA + iB \rightarrow kC + lD \qquad (1)$$

where A, B, C, D, are elements or compounds and h, i, k, l are integers. The rate of formation of C can then be represented by:

$$\frac{dc}{dt} = ka^h b^i \ldots \qquad (2)$$

where: a, b, c, d = concentrations of A, B, C & D

t = time

k = the rate constant

In special cases where there is poisoning or autocatalysis the concentration of C and D may appear in the kinetic equation.

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*Subsequently continuous flow stirred tank reactor will be referred to as CFSTR.

The quantity of C which formed after a time interval t is obtained by integration of Equation (2) so that:

$$t = \frac{1}{k} \int \frac{dc}{a^h b^i} \tag{3}$$

In many cases this integral is not evaluated easily; therefore, for these cases the determination of reaction order and rate by analysis of the system at various time intervals poses a difficult, if not impossible, problem.

If the same reaction is carried out in a tubular reactor where the reactants are introduced together at a steady rate, where the products are removed at a corresponding rate and where there is no accumulation in the system, the steady state is attained soon. After the system reaches steady state, the concentration of A and B at any point in the system remains constant throughout the duration of the process or until a change in any of the process variables is made. Also assume that the flow is the same at all points such as in an isothermal process where no volume change occurs or such as a reaction which takes place in a sufficiently dilute solution. Then, the time for a given element of fluid to traverse a distance along the tube is given by:

$$t = \frac{sL}{u} \tag{4}$$

where: t = time

s = cross section of tube

L = distance traveled

u = volume flow rate

The volume element is considered as an infinitesimally small batch reaction system; therefore, as much reaction occurs in the element after it has passed through a distance L, as would have occured in time t if it had been in a batch system. Substituting equation (4) into equation (3) gives:

$$L = \frac{u}{ks} \int \frac{dc}{a^h b^i} \tag{5}$$

It may be noted that the concentrations of A and B at any given point are stationary and vary with length along the tube according to equation (5). This equation is of the same form as equation (3) for the simple batch reaction and no greater simplicity has been achieved. Analysis of the system at various distances along the tubular reactor gives the same information as analysis at various times after starting of a batch reaction.

Now consider the same reaction carried out in a CFSTR. The stationary state in the CFSTR is expressed by:

$$\frac{da}{dt} = \frac{db}{dt} = \frac{dc}{dt} = \frac{dd}{dt} = 0 \tag{6}$$

where: a, b, c, d, = concentrations of A, B, C, D respectively

t = time

The quantity of C leaving the reactor and the rate at which C is formed is uc, where u is volumetric flow rate and c is the concentration of C. Then, if V is volume of reactor, the quantity of C formed per unit reaction volume per unit reaction time is: $\frac{uc}{V}$ which by definition is equal to the velocity of the reaction. Therefore:

$$\frac{uc}{V} = ka^h b^i \qquad (7)$$

If this equation is compared with equation (3) for the batch system it is apparent that concentration of the product C in the partially reacted system is determined by an equation which does not contain an integral. Thus it is concluded that rate constants and order of chemical reaction may be determined by utilizing equation (7), a simple algebraic expression. For complex reactions the integrals resulting from analysis by the batch or tubular reaction systems may be extremely difficult or impossible to solve analytically.

Denbigh, Stead and Page (9) in a later article presented a design for an experimental apparatus for determining the rates of the liquid phase hydrolysis of ethyl acetate. Apparatus designed as a result of these experiments consisted of a reaction vessel of about 400 cc capacity made in the form of a short cylinder with windows at both ends for optical observation, two large aspirators as reservoirs for the reactants and a 3000 rpm synchronous motor stirrer. Each reactant was fed into the reactor at separate points by passing through a thin walled glass coil which was submerged along with the reactor vessel in a thermostat. The products flowed out through a capillary overflow and to the drain except during the taking of samples. The flow rates of the reactants were controlled by capillaries in inflow tubes which were vented to atmosphere to prevent syphoning. The flow rates through the capillaries were determined by the constant differences in level of solutions at two points which were open to the atmosphere.

The reaction vessel used for the hydrolysis of ethyl acetate was a

spherical Pyrex vessel which had three flattened regions on its walls to prevent liquid from rotating as a mass and thus to facilitate mixing.

To determine minimum mixing time several blade configurations were tested at various mixing speeds. Extrapolation of this data indicated that mixing should occur in less than 0.1 seconds. To confirm sufficient mixing under conditions of flow as used in the continuous flow apparatus a continuous flow of dilute sodium hydroxide solution was introduced into the reaction vessel, initially full of water. Samples of the outflow were collected at intervals and the concentration of sodium hydroxide determined. If the sodium hydroxide took a particular path through the reaction vessel from inlet to outlet the concentration of the outflow would rapidly become equal to the inflow concentration. If, however, the mix were perfect the final concentration would be approached asymptotically by the progressive "dilution" of the residual water in the reactor by the inflow of sodium hydroxide solution. Then if u is the volumetric flow rate of solution and x_o is the concentration of sodium hydroxide in inflowing stream the constant rate of inflow of sodium hydroxide is ux_o (mols /second). At time t let the concentration in outflow be x so the corresponding rate of outflow is ux. Then it follows that at time t the sodium hydroxide is accumulating in the reactor at rate $(ux_o - ux)$ mols per second or at a rate of $\frac{u}{V}(x_o - x)$ mols per second per unit volume, where V is volume of solution in reactor. This is the rate of increase of internal concentration which, according to the perfect mixing hypothesis, is uniform and equal to x, the concentration in the outflow:
hence,

$$\frac{dx}{dt} = \frac{u}{V}(x_o - x) \qquad (8)$$

therefore,

$$\ln \frac{x_o}{x_o - x} = \frac{ut}{V} \tag{9}$$

or,

$$\ln (1 - r) = - \frac{u}{V} t \tag{10}$$

where r equals x/x_o, the concentration in the outflow as a fraction of the inflow concentration. A tabulation of theoretical values of r calculated from equation (10) and a tabulation of values determined experimentally showed excellent agreement between the theoretical and experimental values. The reactor used in these experiments was 602 cc capacity instead of the 400 cc capacity of the finally designed apparatus and the rate of flow of sodium hydroxide was 19.4 cc/minute. The nominal retention time was therefore 602/19.4 which equal 31.1 minutes. From this experiment it was concluded that the system was within 0.1 per cent of final steady state after four hours running. This is a period of time about eight times greater than the retention time.

Young and Hammett (10) considered this problem from a different point of view and arrived at essentially the same solution. Their approach will be discussed in some detail later.

To test the suitability of the CFSTR for the measurements of rate of reaction, Denbigh et al. (11) investigated the alkaline hydrolysis of ethyl acetate. In summary, a solution of ethyl acetate was contained in one reservoir and a solution of CO_2-free sodium hydroxide was contained in another. All air entering the reactant reservoirs and in contact with

the solution at the "breathing points" was CO_2-free.

At the start of an experiment the reactor, was filled with distilled water which was gradually displaced by the flow of the reactants. After the composition had become constant several analyses of the overflow were made. The samples were collected in weighed flasks which contained a small excess of 0.01 N HCl in order to stop the reaction. The samples were weighed and back titrated with barium hydroxide until neutral to cresol-red.

Let x_o and y_o be the initial normality of alkali and ethyl acetate respectively and x and y the normality in the reactor at time t. The flow rate of alkali and ethyl acetate is designated respectively as u_x and u_y. Provided there is no volume change in the reactor then $u_x + u_y$ equals u where u is the outflow from the reactor vessel. Therefore the hydroxyl ion enters the reactor at a constant rate of $u_x x_o$(gram ions per second) and it is removed by the process of chemical reaction in the reactor and of mass transfer of unreacted ions in the outflowing solutions. The rate of removal by mass transfer at time t is ux (gram ions per second). The rate of the chemical process is kxy grams ions reacted per second per liter of reaction space. In the whole volume, V, of reaction space, the rate of reaction is Vkxy (gram ions per second). Therefore the rate of accumulation of hydroxyl ion in the vessel is $u_x x_o$-ux-Vkxy. The rate of increase of concentration was obtained by dividing by V, thusly:

$$\frac{dx}{dt} = \frac{u_x x_o - ux}{V} - kxy \qquad (11)$$

As the system approaches steady state dx/dt approaches zero in the limit, so that:

$$\frac{u_x x_o - ux}{V} - kxy = 0 \tag{12}$$

The corresponding equation for ethyl acetate is:

$$u_y y_o - \frac{uy}{V} - kxy = 0 \tag{13}$$

From these equations k was obtained by eliminating y, giving:

$$k = \frac{u(u_x x_o - ux)}{Vx\,(u_y y_o - u_x x_o + ux)} \tag{14}$$

Therefore, the rate constant k for this reaction can be evaluated from (14), a simple algebraic equation.

For purpose of error analysis equation (14) was simplified by assuming as an approximation $u_x = u_y = u/2$. The equation reduced to:

$$k = \frac{u(x_o - 2x)}{Vx\,(y_o - x_o + 2x)} \tag{15}$$

It was noted that errors in u and V give rise to equal per cent errors in k. From an analysis of the partial derivatives it was found that errors in $x_o y_o$ and x give larger errors in k than the same errors in u and V give, but that by suitable choice of the variables the factor can be made not to exceed two times the error due to u and V.

The result of 11.0×10^{-2} for k using sodium hydroxide as the alkali was compared with the value of 10.8×10^{-2} obtained from the

literature (12). The remainder of the measurements made with $Ba(OH)_2$ gave a mean value of 10.0×10^{-2} which is eight per cent lower than for sodium hydroxide. Since no accurate measurements with $Ba(OH)_2$ were available no direct comparisons could be made; however, measurements in the literature at 9.4° C found the k for $Ba(OH)_2$ to be seven per cent lower than for sodium hydroxide. It was concluded that this method would give rate constants which are correct to within one to two per cent.

Based on this work it was concluded that this method is suitable for use in reaction kinetics and is capable of further refinements with the limitations that fairly large quantities of reagents are required and that the procedure is slow.

Denbigh's suggestion for the use of the CFSTR to measure the kinetics of chemical reactions remained unnoticed, since nothing was published after his articles until 1950 when three papers appeared written by Hammett and his students. The first paper, by Hammett and Young (13), considered the problem of the amount of reactants which must flow to waste. The problem was analyzed specifically for the alkaline bromination of acetone using the following symbols:

a, b, c = Concentration of reactants in the reactor at steady state, mols/liter

x, y = Concentrations of reaction products in reactor at steady state, mols/liter

a_o, b_o, c_o = Concentration of reactants in entering liquid, mols/liter

x_t, y_t = Concentration of reaction product at time t, mols/liter

t = Time, minutes

u = Total flow rate

V = Reactor volume, liters

γ = Degree of conversion in steady state i.e., x/a_o or x/b_o whichever is larger.

τ = No. of multiples of reactor volume which have traversed the system i.e., tu/V

$\rho = b_o/a_o$ *

r = Rate of reaction

k, k' = Rate of constants

In this analysis a refers to acetone, b to sodium hydroxide, c to hypobromite, x to bromoform and y to carbon tetrabromide.

The analysis is based on the assumptions that the stoichiometric equation for the bromination reaction can be represented by:

$$(CH_3)_2CO + 3BrO^- \rightarrow CHBr_3 + CH_3CO_2^- + 2OH^- \qquad (16)$$

and that the rate is proportional to the concentration of acetone and hydroxyl ion and independent of the concentration of hypobromite ion, which are shown to be good enough approximation. The basic equation for approach to steady state is:

$$\frac{dx_t}{dt} = r - \frac{ux_t}{V} \qquad (17)$$

where: r = rate of reaction.

For the bromination based on the assumption presented above the rate is expressed by:

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*In the paper by Hammett and Young ρ was defined as a_o/b_o but a check of the calculation and the original thesis show that this must be in error; therefore, it is corrected to avoid confusion in the presentation of these calculations.

$$r = kab = k(a_o - x_t)\ (b_o + 2x_t) \tag{18}$$

In steady state $\frac{dx_t}{dt} = 0$ and $x_t = x$

So that:

$$k = \frac{u}{V}\ \frac{x}{(a_o - x)\ (b_o + 2x)} \tag{19}$$

Substituting $x = \gamma a_o$ and $b_o = \rho a_o$ gives:

$$k = \frac{u}{Va_o}\ \frac{\gamma}{(a_o - x)\ (\rho_o + 2\gamma)} \tag{20}$$

The variables of interest are τ and x_t/x. To obtain an equation in terms of these variables from equations (17), (18), and (20) some additional steps are added here simply to clarify the analysis.

Note that:

$$\frac{d(x_t/x)}{dt} = \frac{1}{x}\ \frac{dx_t}{dt} \quad \text{or} \quad \frac{dx_t}{dt} = \frac{d(x_t/x)}{dt} \tag{21}$$

and since: $\tau = \frac{tu}{V}$

then:

$$d\tau = \frac{u}{V}\,dt \quad \text{or} \quad \frac{dt}{d\tau} = \frac{V}{u} \tag{22}$$

so that:

$$\frac{d(x_t/x)}{d\tau} = \frac{d(x_t/x)}{dt} \cdot \frac{dt}{d\tau} = \frac{1}{x}\ \frac{dx_t}{dt}\ \frac{V}{u} \tag{23}$$

Substituting in equation (17) gives:

$$\frac{d(x_t/x)}{d\tau} = \frac{1}{x}\,\frac{V}{u}\,\left(r - \frac{u}{V}\,x_t\right) \tag{24}$$

Substituting (18) in the equation above:

$$\frac{d(x_t/x)}{d\tau} = \frac{V}{ux}\,k\,(a_o - x_t)(b_o + 2x_t) - x_t/x \tag{25}$$

Then noting that from equation (20) and $x = a_o\gamma$ that:

$$\frac{V}{ux} = \frac{\gamma}{ka_o x(1 - \gamma)\,(\rho + 2)} = \frac{1}{ka_o^2(1 - \gamma)\,(\rho + 2\gamma)} \tag{26}$$

Upon simplifying, the result presented by Young and Hammett was obtained:

$$\frac{d(x_t/x)}{d} = \frac{\rho + (2\gamma^2 - \rho)\,x_t/x - 2\gamma^2\,(x_t/x)^2}{(1 - \gamma)\,(\rho + 2\gamma)} \tag{27}$$

Since the integral is known, the constant of integration can be evaluated from the initial condition of $x_t = 0$ when $\tau = 0$ which gives:

$$\tau = \frac{(1 - \gamma)\,(\rho + 2\gamma)}{\rho + 2\gamma^2}\,\ln\,\frac{\rho + 2\gamma^2\,(x_t/x)}{\rho(1 - x_t/x)} \tag{28}$$

A plot was presented of $\tau_{0.001}$, which is the number of multiples of reactor volume which must flow through the system in order to bring the product concentration to a value differing by 0.1 per cent from steady state, i.e., to make $x_t/x = 0.999$ for $\rho = 1$. It was concluded from this analysis that the steady state condition can be attained to a high

precision with the expenditure of a volume of reagents a little over seven times the reactor volume in the most unfavorable case. This result is compared to the approximately eight reactor volumes required to reach steady state reported by Denbigh.

The case of consecutive reactions is illustrated by observing that in the example being studied equations (16) and (18) do not give a complete account of bromination of acetone. In addition to reacting with acetone bromoform reacts slowly with hypobromite. The consideration of both the formation of bromoform and this subsequent reaction gives:

$$\frac{u}{V} x = k(a_o - x - y)\,(b_o + 2x + 3y) - k'x \tag{29}$$

as the steady state equation for concentration x of bromoform.

The steady state equation for concentration of carbon tetrabromide is:

$$\left(\frac{u}{V}\right) y = k'x \tag{30}$$

also:

$$c_o - c = 3x + 4y \tag{31}$$

from equations (29) and (30)

$$k = \frac{u}{V}\ \frac{x(1 + k'\,V/u)}{[a_o - x(1 + k'\,V/u)]\,[b_o + x(2 + 3k'\,V/u)]} \tag{32}$$

from (30) and (31)

$$x = \frac{c_o - c}{3 + 4k'\,V/u} \tag{33}$$

The conclusion was made that, since k may be determined by a separate experiment on the rate of bromation of bromoform, the rate constant k of the first step in this system of consecutive reactions may be determined by substitution of easily obtainable experimental quantities in equation (32). If the reaction order of this step were unknown it could be determined easily from the experimentally observed dependence of the reaction rate, r, which is given by:

$$r = \frac{u}{V} (c_o - c) \frac{1 + k' V/u}{3 + 4k' V/u} \qquad (34)$$

on the concentrations of reactants. Thus it was concluded that the determination of reaction orders and rate constants in a system of consecutive reactions of higher orders should offer no special difficulty in a CFSTR, a problem which would be extraordinarily difficult if treated by conventional methods.

The experimental apparatus used by Young and Hammett (14) for the bromination of acetone consisted of two reservoirs which hold the reactants. The reactants flow into the reactor through capillary tubes at a rate held constant by applying a constant pressure to the reservoirs. The reactor has a stainless steel air driven stirrer and overflow tube. The whole system was kept at constant temperature by immersion in a thermostat at 25.00° C.

Experimental data showing the approach to steady state was plotted for three runs. Data for fifteen runs in which steady state was reached were given and values of the rate constant, k, were calculated. The reproducibility of this data is good although k varies over the range of

process variables. It was concluded that the variation of k with changed flow rate and γ is indicative of a real departure of the reaction from accepted kinetics and indicates the importance of this method for rates studies.

Saldick and Hammett (15) in the second paper considered a method of continuously titrating the output from a CFSTR which avoids the difficulty of quenching and analyzing a considerable volume of reaction mixture.

The reaction used for their investigation was the alkaline hydrolysis of an ester. The reactants were introduced in separate streams of constant flow into a closed stirred reactor. Then the partially reacted mixture overflowed into a small titration chamber where it was mixed with an aqueous solution of hydrochloric acid containing an acid-base indicator, the titrating solution. The flow of the titrating was regulated until a visual end-point was observed.

Since some of the reaction took place in the exit tube, the rate constant k was calculated by successive approximations for a value of x' obtained from the flow titration. If the double primes are used to designate the exit tube then $dc''/dt = k(a_o - x'')(b_o - x'')$ in any volume element of liquid moving through the tube. A solution of the differential equation was made using the boundary conditions: at $t' = 0$, $x'' = x$ and $x'' = x'$ at $t' = V'/u$.

$$x = \frac{x' = (P - 1)\,(a_o - x')\,(b_o - x)}{(P - 1)\,x' + b_o + a_o P} \qquad (35)$$

where: $P = \exp\,(b_o - a_o)\,k\,V'/u$.

From an estimated value of k in equation (35) a value of x was obtained which gave a better value of k when substituted in:

$$k = \frac{ux}{V} (a_o - x) (b_o - x) \qquad (36)$$

which in turn gave an estimate of k' which was used to obtain a better value of x. They found that two successive approximations were usually enough since only about three per cent of the total reaction took place in the exit tube. Their estimates of precision were 0.1 per cent for flow measurements and 0.1 per cent for the volume of the reactor and exit tube. It was found that a flow error of 0.1 per cent in each of the experimental measurements would lead to an overall precision measure of about 1.0 per cent for the rate constant k.

The rate constants were calculated and corrected to 25.00° C, using 10.9 kilocalorie per mol for energy of activation of ethyl acetate and 11.5 kilocalorie per mol for ethyl α - hydroxyisobutyrate. These corrections amounted to less than 0.4 per cent in most cases since the steady temperature was usually within 0.06° C of 25.00° C. From a summary of older literature an average value of 6.46 (16) with a range up to 6.94 was found for the rate constant for the ethyl acetate reaction. This compares with a value of 6.750 $\pm$ 0.75 per cent which Hammett and Saldick (17) determined by CFSTR technique and a value of 6.60 which they obtained from Denbigh using a CFSTR with batch-wise titration.

The value for the hydroxyisobutyrate rate constant differed considerably from the value reported by Salmi and Leimu but it was in satisfactory agreement with the value 9.02 obtained by the batch technique.

The third of these papers, written by Rand and Hammett (18), reported the development of apparatus and methods for measurement of reaction rate through the determination of the temperature rise in a CFSTR. The measure of temperature rise has been used to measure reaction rates in nonflow systems but it is complicated by the change in specific rate as temperature changes. This is not true with the CFSTR since all the reaction occurs at a single temperature, that of the reactor.

In this analysis it was assumed that the heat evolved is strictly proportional to the extent of reaction, that the heat capacity of the system is unchanged by the reaction, and that heat losses from the reactor by radiation and conduction at any fixed flow rate are proportional to the temperature gradient from the reactor to its surroundings. These assumptions are accurate enough for practical experiments provided the solutions are dilute and the temperature gradients are small.

On this basis a heat balance was set up across the reactor at steady state:

$$H_o u + h_1 + h_2 u + \Delta H(a_o - a)u^* = (H_o + C\Delta T)u + h_3 \qquad (37)$$

where: H_o = Heat content of reactants at thermostate temperature, cal/liter

h_1 = Heat of stirring, cal/min.

h_2 = Heat of mixing at a given flow rate, cal/liter

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*Equation from original paper reporduced this term as: $\Delta H(a_o - a)$; however, a check of units reveals that this is inconsistent with the other terms without multiplying it by u.

h_3 = Heat loss from cell due to radiation conduction, etc. cal/min

ΔH = Heat evolved per mol of ester reacted, cal/mol

a_o = Concentration of reactant in entering liquid, mol/liter

a = Concentration of reactant in reactor at steady state mol/liter

C = Average heat capacity of cell content over range T, cal/^oC-liter

T = Observed steady state temperature rise, ^oC

u = Volumetric flow rate, liters/min

Then by definition:

$$\Delta T' = \Delta T - \frac{h_1}{Cu} - \frac{h_2}{C} - \frac{h_3}{Cu} \tag{38}$$

and the equation for a second order reaction in steady state of CFSTR is:

$$(\frac{u}{V})\ (a_o - a) = ka(b_o - a_o + a) \tag{39}$$

This reduces to:

$$\Delta T' = \frac{\Delta H}{2C}\ (a_o + b_o + \frac{u}{kV}) - \sqrt{(a_c + b_o + \frac{u}{kV})^2 - 4a_o b_o} \tag{40}$$

It was reported that no practical way was found to obtain the quantities $\frac{\Delta H}{C}$ and k from experimental data; therefore the special case was considered where a_o and b_o differed by a few per cent. Equation (39) is replaced by:

$$\frac{u}{V}(a_o - a) = k(c_o - a_o + a)^2 \tag{41}$$

with an error in k of 0.005 per cent when a_o and b_o differed by three per cent. Then from equations (37), (38) and (41):

$$\sqrt{u\Delta T'}/c_o = \sqrt{\frac{V\Delta H}{C}}\sqrt{k}\,(1 - C\Delta T'/\Delta H c_o) \tag{42}$$

Then with:

$$k = \bar{k} + (\frac{dk}{dT})\delta T \tag{43}$$

where $\bar{k}$ is the k at the average steady state temperature of a series of experiments at varying flow rates and δT is the difference between steady state temperature and this average.

$$\sqrt{k} = \sqrt{\bar{k}}\sqrt{1 + \frac{d(\ln k)}{dT}\delta T} = \sqrt{\bar{k}}\left\{1 + \frac{d(\ln k)}{dT}\delta T + \ldots\right\} \tag{44}$$

Substituting (44) in (42):

$$\frac{\sqrt{u\Delta T'}/c_o}{1 + \frac{1}{2}\frac{d(\ln k)}{dt}\delta T} = \sqrt{\frac{V\Delta H k'}{C}}\,(1 - \frac{C\Delta T'}{\Delta H c_o}) \tag{45}$$

Then since the denominator on the left hand side represents the correction factor for the variation of k with temperature which seldom differed from unity by more than 0.3 per cent in these experiments it could be neglected for a good first approximation if no estimate for d(ln k)/dt is available. Then by plotting the left hand side of (45) vs $\Delta T'/c_o$ a straight line is obtained whose slope is $-\sqrt{V\bar{k}C/\Delta H}$ and whose intercept at

$\Delta T'/c_o = 0$ is $V\Delta H\bar{k}/C$. The product of this slope and intercept is $-V\bar{k}$ from which $\bar{k}$ is determined. At the other intercept where $u = 0$:

$$\sqrt{\frac{V\Delta H\bar{k}}{C}} = \sqrt{\frac{VC\bar{k}}{\Delta H}} \quad \frac{\Delta T'}{c_o} \tag{46}$$

or:

$$\frac{\Delta H}{C} = \frac{\Delta T'}{c_o}$$

so that the intercept on the absissa is $\Delta H/C$.

The inclusion of the $d(\ln k)/dt = 0.064$ in the plot of equation (45) resulted in a maximum change of 0.3 per cent.

To see if this method could distinguish between first and second order reactions, runs at lower concentrations were included, with an added correction due to differences in $\Delta H/C$ so that all the data could be included on the same coordinates. The data were plotted according to equation (45) and according to:

$$\frac{a_o}{\Delta T'} = \frac{C}{\Delta H} + \frac{C}{kV\Delta H}\, u \tag{47}$$

which is applicable if the reaction is first order. From these two plots, it was concluded that equation (45) is followed and therefore, the technique distinguishes between first and second order reactions.

Then by the method of least squares the slope was calculated. The intercept at $\Delta T'/c_o = 0$ was determined, from which $\bar{k} = 9.33 \pm 0.10$ liter per mol-minutes at 25.73° was calculated. This was corrected by $d(\ln k)/dt$ to give $k = 8.90$ at $25.00^\circ C$. This value was compared to

8.90 $\pm$ one per cent which was obtained by continuous titration and a value of k = 9.02 $\pm$ 1.2 per cent which was obtained from a batch determination. From this experiment it was concluded that this experimental technique provides a method which gives accurate rate constants for quite rapid reactions.

In 1956 Hammett and Humphreys (19) published another paper on the subject of CFSTR in which they considered fast reactions. It was found that when one of the reactants was injected as a pure liquid or as a concentrated solution by a hypodermic syringe driven by a constant speed screw, the CFSTR technique could be used on reactions with half-times as short as 0.6 seconds. The reactions rate constants for the alkaline hydrolysis of methyl and ethyl formate were calculated from the data obtained using this technique.

The review of the literature is concluded with Hammett and Burnett's (20) paper published in 1958 in which they considered the applicability of the CFSTR technique to kinetic studies of complex reactions involving medium effects. To demonstrate these effects the alkaline hydrolysis of diethyl succinate was used. This type reaction may be represented by the following equations:

$$A + B \xrightarrow{k_1} C + E \qquad (48)$$

$$B + C \xrightarrow{k_2} D + E \qquad (49)$$

It was concluded that the specific rate for the first saponification step k_1, is subject to a primary salting effect which is specific to the succinate ion formed during the reaction. The rate is decreased with

increasing succinate ion concentration, the magnitude of the decrement at the same time is dependent upon the sodium ion concentration in the reacting medium. The specific rate for the second step, k_2, exhibits a positive salt effect with increasing sodium ion concentration. The salt is not determined by ionic strength.

The literature, although limited, reveals that the CFSTR has been used to determine accurately the chemical reaction rate constants of a variety of homogeneous liquid phase reactions. Although no papers were found which dealt with the use of the CFSTR method to determine the rate constants of homogeneous gas phase reactions it is concluded from this review that such a system is theoretically possible since the mathematical analysis for liquid phase and gas phase reactions are identical.

The advantages of the CFSTR system revealed by this literature review are: (1) the simplicity of the equations from which the rate constants are calculated as compared with the batch or tubular flow methods, i.e., a simple algebraic equation for the CFSTR system versus an integral equation for the tubular flow or batch systems. (The mathematical simplicity of the CFSTR is a particularly important advantage in the calculation of rate constants of consecutive or complex reaction since the batch or tubular flow reactors require the solution of an integral equation which in most cases, can only be solved by tedious approximation methods.) (2) Reaction rates can be determined for very fast reactions. (3) Reactions can be studied under constant conditions at any stage of the reaction process since the rate of change of the concentration of all constituents is zero at steady state.

CHAPTER III

DESIGN OF A CFSTR FOR GAS PHASE REACTIONS

Since the literature search revealed only CFSTR systems for liquid phase reactions, a design for a system which can be used for homogeneous gas phase reactions is presented here.

Basically the design for a gas phase CFSTR system is the same as the liquid phase CFSTR systems which have been reviewed in Chapter II. However, the problems of supplying the reactants, controlling and measuring the flow rates and concentrations of both reactants and products are much more difficult for gases than for liquids. For some specific reactions it might be necessary to operate the system at high pressure in order to keep the reactor volume small enough so that outflow of chemicals to waste while the reaction approaches steady state is not excessive.

From the block diagram of the CFSTR in Figure 1 it is seen that the system is made up of three major divisions:

(1) reactant supply

(2) reactor

(3) product removal and analysis

The function of the reactant supply part of the system is to supply measured amounts of extremely pure reactants to the reactor at the proper temperatures and pressure. A specific design of the reactant supply section is dependent upon the reaction being studied. The reactants for many reactions can be supplied from standard gas cylinders.

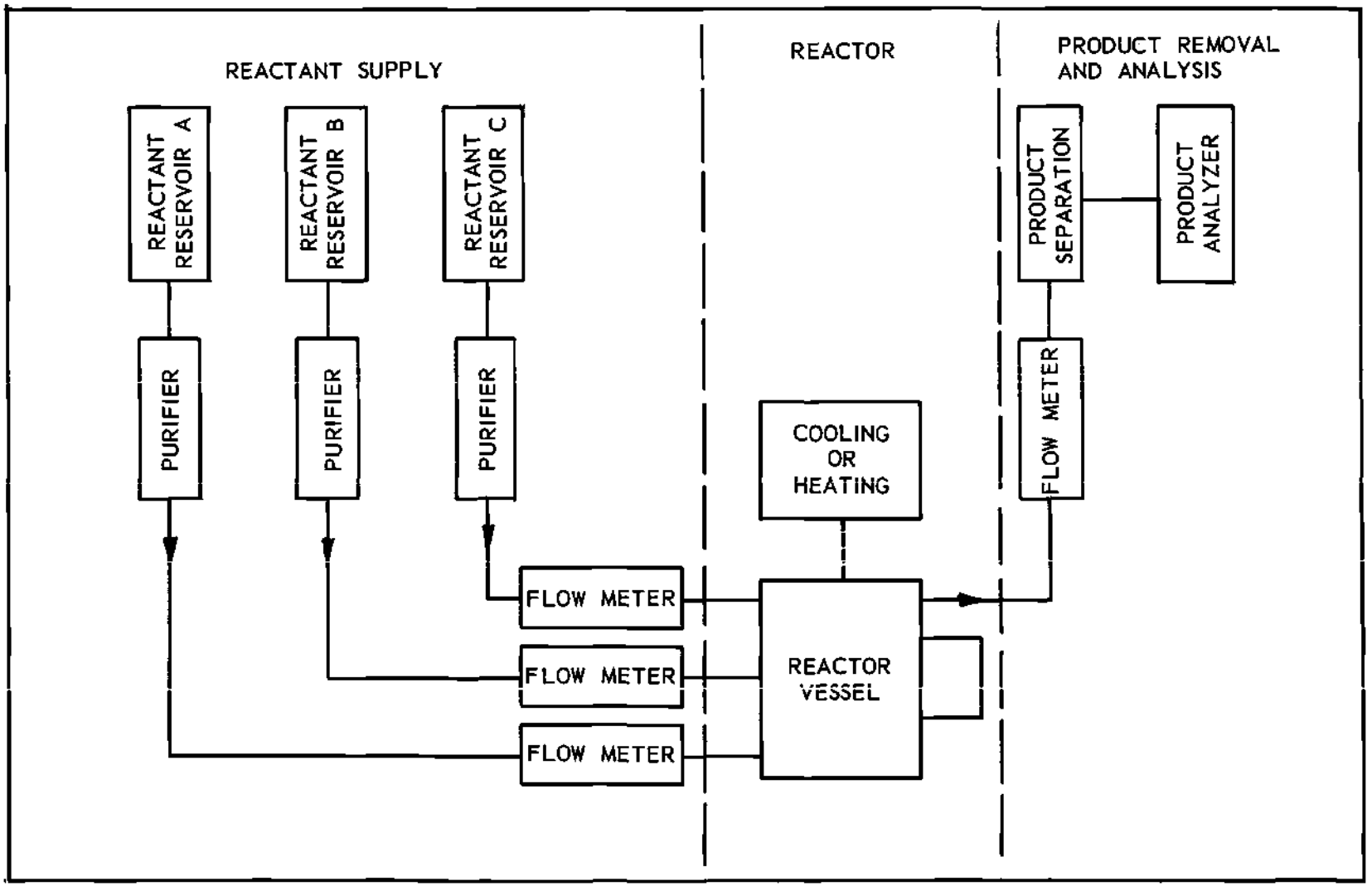

Figure 1. Block Diagram of a CFSTR System.

For substances which are not available in cylinders or are not gases at room temperatures some form of generator would have to be used. The reactants flow from their reservoir through a purification apparatus, if necessary, a thermostat, flow meter and into the reactor vessel.

The function of the reactor vessel is to receive reactants at a constant temperature and pressure such that a reaction will occur and to mix these materials so that the concentration through the vessel is constant. To maintain a constant temperature some provision must be made to introduce heat into the reactor or to remove heat from the reactor for the duration of the experiment.

The product removal and product analysis part of a CFSTR is concerned with measuring the volumetric flow rate of the product stream, quenching the reaction so that no additional products are formed after the reactants have left the reactor and determining the extent of the reaction by analyzing the outflow for the concentrations of the constituents. Specific designs for this part of a CFSTR system again must depend upon the particular reaction being studied. However, because of the characteristics of the CFSTR system, some form of volumetric analysis will probably be most suitable. For example, reactions which produce acids or bases can be quenched and analyzed by passing the outflow through a basic or acid solution of known concentration and then to back titration to determine the product concentration. A more sophisticated method such as described by Hammett and Saldick (21) would be to continuously titrate the outflow. Any method of separating the reactants or products such as selective adsorbtion will quench the reaction. Rapid cooling of the outflow can also quench a reaction by slowing the reaction

rate until it is effectively zero or by condensing one or more of the reactants, thus permitting separating from the other materials. Analysis can be made along with the quenching procedure as in case of neutralization of acid or base or it can be a separate process after the products are separated.

In addition to standard volumetric analysis, chromotography and thermal conductivity cells are two other important methods which may be adapted to determine rpoduct concentrations.

A design of a CFSTR system for the reaction between methane and sulfur vapor at one atmosphere and at 550-625° C is proposed. This reaction was carried out under these conditions by Smith and Fisher (22) using a tubular type reactor. The rate constants which Smith and Fisher calculated are used as basis for the design of the CFSTR system and can be used to evaluate the design if the equipment is built.

A flow diagram of the proposed CFSTR system is presented in Figure 2. Methane is supplied from a standard cylinder. The methane passes from the cylinder through a purification train (anhydrous calcium sulphate and copper foil), through a suitable flow meter, through a preheater and into the reactor vessel.

Sulfur vapor is supplied from a generator similar to the one used by Fisher and Smith (23) in which liquid sulfur, maintained by a thermostat at its melting point, is delivered, through a tube which is open near the bottom of the sulfur reservoir, to a vaporization section by regulated air pressure. The liquid is vaporized when it comes into the short length of the tube which is heated with resistance wire wrapped around a short length of the tube. The sulfur vapor then passes through

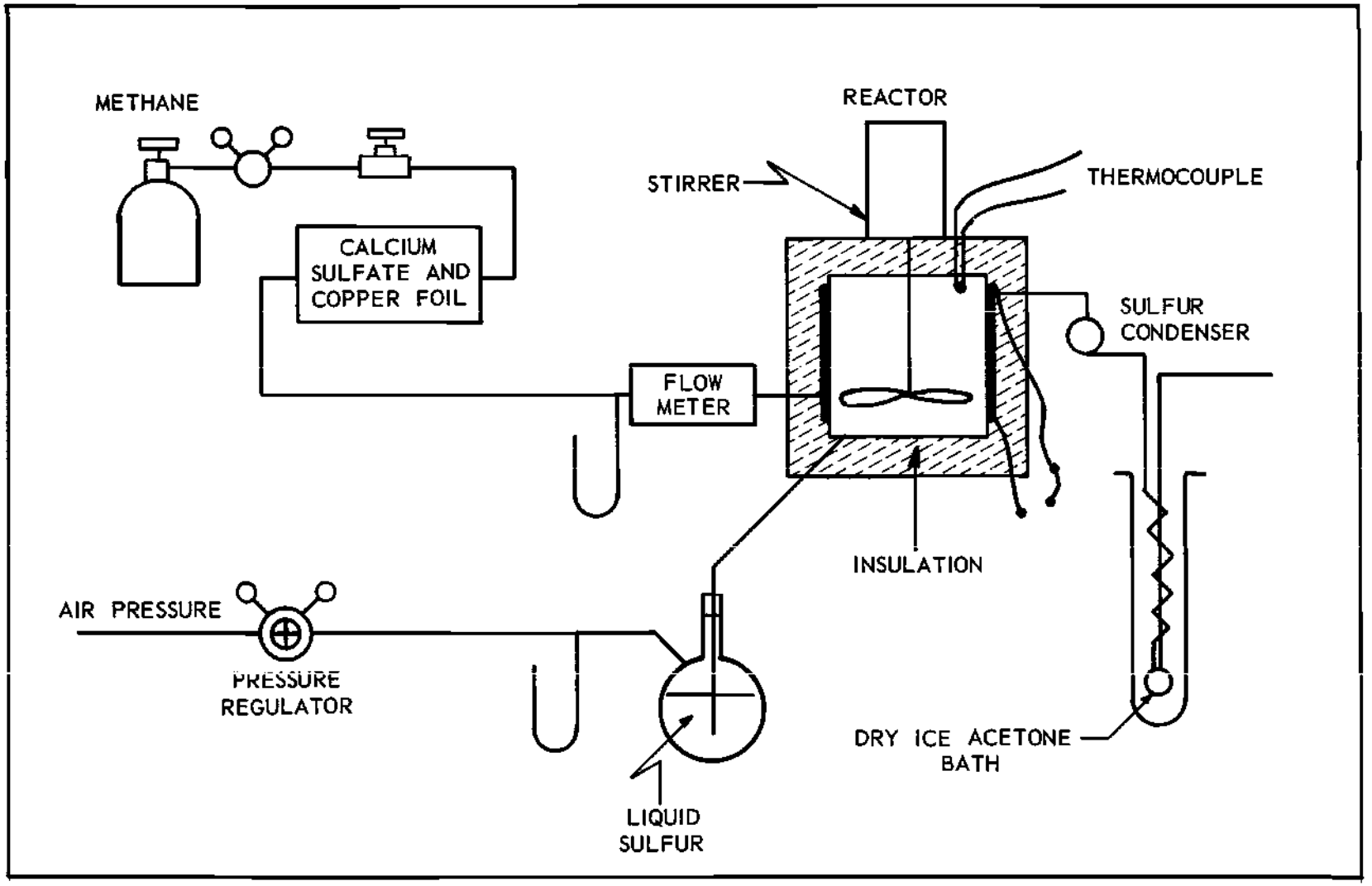

Figure 2. Flow Diagram of CFSTR System for the Methane-Sulfur Reaction.

a capillary tube through the preheater and into the reactor. The sulfur vapor generator tends to be self stabilizing, since variations in the interface level are automatically reduced by the differences of heat transfer to the liquid and gas. If the liquid level rises, the additional heated surface covered by liquid increases the heat transfer and the liquid is vaporized more rapidly, tending to increase the pressure which causes the liquid level to decrease. When the liquid falls, less heater surface is exposed to the liquid; therefore, the heat transfer decreases, which decreases the pressure and therefore causes the liquid level to increase.

In the reactor vessel the reactants are rapidly mixed with a ducted propeller driven by a one-fourth horsepower motor and the reaction allowed to proceed at constant temperature and pressure. The mixture of gases leaves the reactor vessel and passes through a flow meter into a sulfur condenser which removes the unreacted sulfur. Any divided sulfur in the exit gas stream is removed by a glass wool filter before the mixture goes into a carbon disulfide condenser. Carbon disulfide is continuously extracted from the product gases in the condenser by cooling to -60° C where essentially all of it condenses. The remainder of CS_2 in the gas phase is estimated from its vapor pressure at -60° C and the condensate analyzed for CS_2 according to the xanthate oxidation method of Bell and Gruss (24).

The volume of the reactor vessel was determined by the following analysis:

Consider the reaction:

$$CH_4 + 2S_2 \rightarrow CS_2 + H_2S \qquad (50)$$

If this reaction is second order with respect to methane and S_2 then:

$$\frac{u}{V} C_1 = kC_3 C_4 \tag{51}$$

where:

u = volumetric flow rate, liters/hour

V = reactor vessel volume, liters

k = rate constant, liter/(gm mol)(hr)

C_1 = concentration of CS_2, mols/liter

C_3 = concentration of CH_4, mols/liter

C_4 = concentration of Sulfur, mols/liter as (S_2)

Then assuming the conversion that would result from the reaction of 0.02, 0.2, 0.4, 0.6, 0.8 mol fraction of methane the concentrations of CH_4, S_2 and CS_2 present in the reactor and consequently the outflow were calculated and tabulated in Table 1. Using these values of concentrations the total volumetric flow rate from the reactor was calculated for several reactor volumes. These flow rates are tabulated in Table 2 and plotted in Figure 3.

Since Denbigh and Hammett both confirmed that steady state in a CFSTR is reached with a maximum expenditure of reagents equal to eight times the volume of the reactor vessel, a small reactor vessel is desirable to minimize the amount of chemical which are used in each experiment. However, when the reactor vessel volume is small the volumetric flow rate is also small. The absolute value of the flow rate for a given reactor volume is dependent upon the rate of reaction of the particular reaction being studied. Consideration must also be given to the necessity to

Table 1. Concentration x 10^4 of Reactants and Products for Specific Conversions

Temperature (°C)		Conversion, Fraction CH_4				
		0.02	0.2	0.4	0.6	0.8
550	CH_4	48.314	39.44	29.58	19.72	9.86
	S_2	96.628	78.88	59.16	39.44	19.72
	CS_2	0.986	9.86	19.72	29.58	39.44
	H_2S	1.972	19.72	39.44	59.16	78.88
575	CH_4	46.746	38.16	28.62	19.08	9.54
	S_2	93.492	76.32	57.24	38.16	19.08
	CS_2	0.954	9.54	19.08	28.62	38.16
	H_2S	1.908	19.08	38.16	57.24	76.32
600	CH_4	45.668	37.28	27.96	18.64	9.32
	S_2	91.336	74.56	55.92	37.28	18.64
	CS_2	0.932	9.32	18.64	27.96	37.28
	H_2S	1.864	19.02	37.28	55.92	74.56
625	CH_4	44.492	36.32	27.24	18.16	9.08
	S_2	88.984	72.64	54.48	36.32	18.16
	CS_2	0.908	9.08	18.16	27.24	36.32
	H_2S	1.816	18.16	36.32	54.48	72.64

Table 2. Total Volumetric Flow Rate for CFSTR in Liters per Hour

$V_{(liters)}$	Temp.	Conversion, fraction CH_4 0.02	0.2	0.4	0.6	0.8
0.25	550	2,651	176.7	49.69	14.72	2.76
	575	1,246	83.04	23.35	6.92	1.30
	600	756.3	50.40	14.18	4.37	0.79
	625	414.4	27.60	7.763	2.30	0.431
0.5	550	5,303	353.4	99.39	29.44	5.52
	575	2,502	166.7	46.88	13.89	2.60
	600	1,513	100.8	28.35	8.40	1.58
	625	828	55.2	15.53	4.60	0.862
0.75	550	7,954	530.0	149.1	44.17	8.28
	575	3,748	249.7	70.23	20.81	3.90
	600	2,265	150.9	42.44	12.57	2.36
	625	1,238	82.5	23.21	6.88	1.29
1.0	550	10,606	705.7	198.78	58.89	11.04
	575	4,994	332.8	93.59	27.73	5.20
	600	3,021	201.3	56.62	16.77	3.15
	625	1,657	110.4	31.05	9.20	1.73
1.5	550	15,909	1,060.0	298.2	88.33	16.56
	575	7,469	497.6	140.0	41.47	7.78
	600	4,520	301.2	84.72	25.10	4.71
	625	2,485	165.6	46.58	13.79	2.59

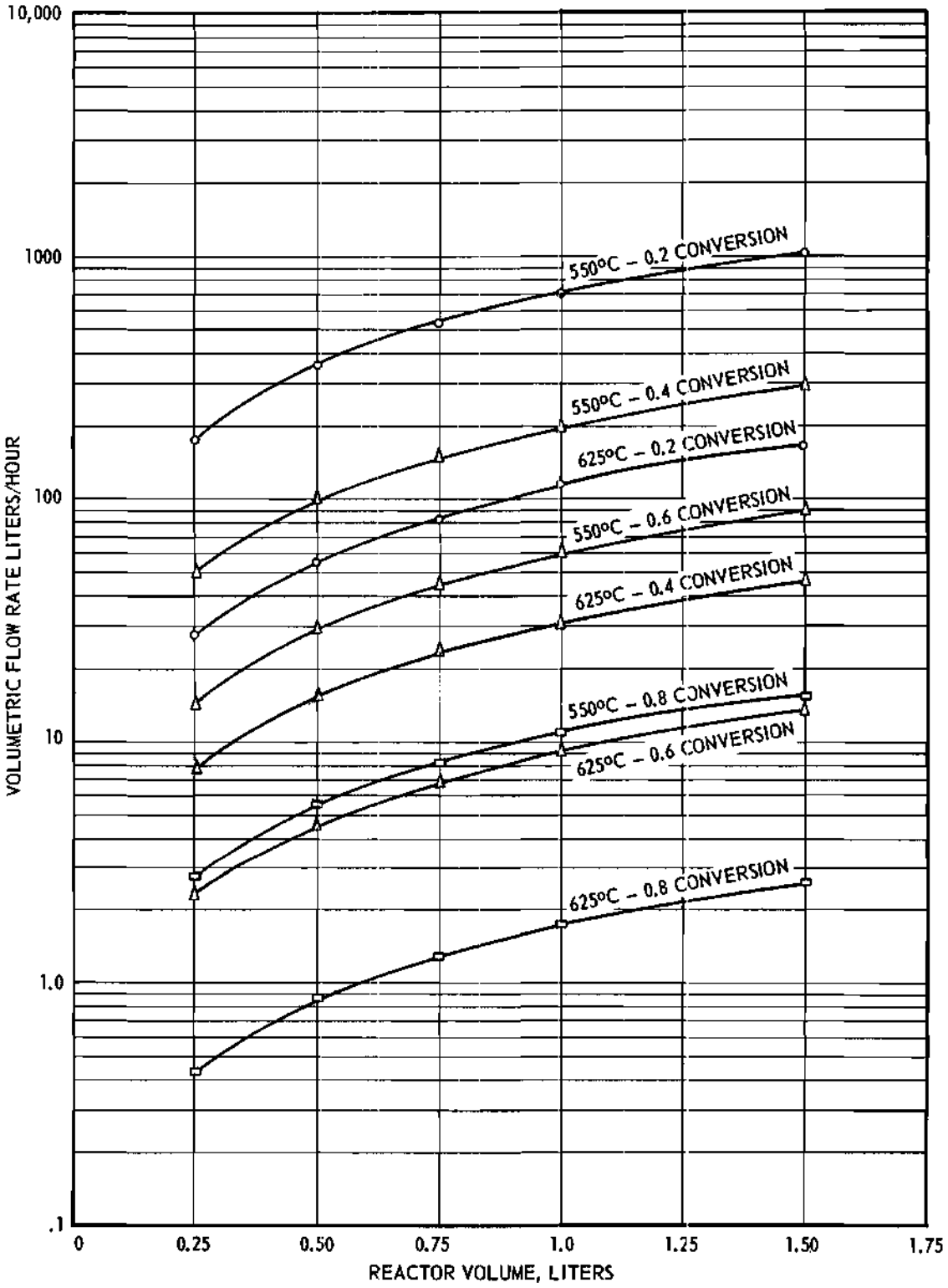

Figure 3. Total Volumetric Flow Rate Versus Reactor Volume for the Methane-Sulfur Reaction.

provide mixing inside the reactor and to provide heating and cooling so that the reaction temperature can be controlled. From the plot of flow rate vs. reactor volume it was decided that for the methane-sulfur reaction at temperatures of 550-600° C a reactor volume of one liter would be large enough to include the necessary heating or cooling and stirring equipment. Also this volume is sufficiently large so that the minimum flow rate is not too small to be measured with a standard flow meter yet the volume is sufficiently small so that the maximum flow rate is not impractically high and the expenditure of chemicals to reach steady state is not excessive.

The shape of the reactor vessel was chosen to be a cylinder with its height equal to its diameter since this configuration provided the best solution to the following requirements: (1) the reactants must be rapidly mixed so that the composition through the vessel is essentially constant, (2) the conduction heat losses should be minimized since the reaction between methane and sulfur is endothermic and is to be conducted at temperatures between 550° C and 625° C, and (3) the reactor should be easy and inexpensive to fabricate.

Since:

$$V = \frac{\pi D^2}{4} L \tag{52}$$

where:

V = reactor volume, 1000 cc

D = reactor diameter

L = length, L = D

Then:

$$V = \frac{\pi D^3}{4} \tag{53}$$

$$\text{or} \quad 1000 = \frac{\pi D^3}{4}$$

$$D = \left(\frac{-1000}{\pi}\right)^{1/3} = 10.5 \text{ cm.}$$

The amount of power necessary to maintain this reaction at the specified temperatures was estimated from a heat balance on the system at a maximum flow of 3.9 standard liters per hour and reaction temperature of 550° C.

$$Q_{req} = Q_{out} - Q_{in} \tag{54}$$

where:

Q_{req} = power required

Q_{out} = power absorbed by the heat of reaction, heat dilution, conduction loss from reactor and heat removed with product outflow.

Q_{in} = heat input with reactants

First the heat of reaction was determined.

Consider the reaction:

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S \tag{55}$$

then:

$$\Delta H_r = \Delta H_{f1} + \Delta H_{f2} - \Delta H_{f3} - \Delta H_{f4} \tag{56}$$

where:

ΔH_r = heat of reaction cal/mol CH_4

ΔH_{f1} = heat of formation CS_2, 22.44 k cal/mol (25)

ΔH_{f2} = heat of formation H_2S, - 5.3 k cal/mol (26)

ΔH_{f3} = heat of formation CH_4, - 17.865 k cal/mol (27)

ΔHf_4 = heat of formation S_2, 0

Therefore:

$$\Delta H_r^{18^{\circ}C} = 22.4 + 2(-5.3) - (17.865) = + 39.7 \text{ k cal/mol } (CH_4)$$

But:

$$\Delta H_r^{550^{\circ}C} = \Delta H_r^{18} + \int_{18}^{550} \Delta Cp \, dT \tag{57}$$

where:

$$\Delta Cp = (Cp_1) + 2(Cp_2) - (Cp_3) - 2(Cp_4)$$

and:

Cp_1 = heat capacity at constant pressure, CS_2, 1.9 cal/mol° C (28)

Cp_2 = heat capacity at constant pressure, H_2S, .105 cal/mol° C (29)

Cp_3 = heat capacity at constant pressure, CH_4, 9 cal/mol° C (30)

Cp_4 = heat capacity at constant pressure, S_2, 16 cal/mol° C (31)

Assuming the values of Cp are independent of temperature then:

$$\Delta Cp = 11.9 + 2(10.5) - 2(9) - (16) = -1.1$$

and

$$\Delta H_r^{550^{\circ}C} = 39.7 + (-1.1)\ (550-18) = 39.2 \text{ K cal/mol } CH_4$$

The maximum flow of 3.9 liters/minute occurs at conversion 0.2 mol fraction methane and temperature 550°C. One third or 1.3 liters/minute represents flow of methane since the reactants input is in stoichiometric proportion.

$$Q_r = n_3\ \Delta H_r \tag{58}$$

where:

Q_r = power absorbed by reaction, watts

n_3 = mols CH_4 reacted, $(\frac{1.3 \times 0.2}{22.4})$, mols

ΔH_r = Heat of reaction, (39.2 x 69.8), watts/mol CH_4

Substituting in equation (58) gives:

$$Q_r = \frac{(1.3)\ (0.2)\ (39.2)\ (69.8)}{22.4} = 32.2 \text{ watts}$$

The heat of dilution and mixing was estimated by assuming that all the sulfur is initially formed as S_8 and then dissociates into S_2 with the absorption of 95K cal per mol of S_8 (32). The maximum flow rate of sulfur is 2.6 liters/minute of S_2 which will require:

$$Q_d = n_5\ \Delta H_d \tag{59}$$

where:

n_5 = mols S_8, $\frac{2.6}{(4)\ (22.4)}$

ΔH_d = Heat absorbed per mol S_8, (95 x 69.8), watts/mol

So:

$$Q_d = \frac{(2.6)(95)(69.8)}{(4)(22.4)} = 190 \text{ watts.}$$

The maximum heat loss due to the removal of the unreacted reactants and products was estimated from the following:

The mole fraction of the constituents of the outflow was estimated for the maximum flow condition of 3.9 liters/minute at standard conditions and a molal heat capacity of the outflow from the following equation:

$$\sum x_i \; Cp_i = Cp^* \tag{60}$$

where:

x_i = mol fraction of i^{th} constituent in outflow

Cp_i = heat capacity of i^{th} constituent

Cp^* = heat capacity of outflow

Cp^* = (0.27) (16.0) + (0.06) (11.9) + (0.13) (10.5)

= 11.3 cal/mol$^\circ$ C

Then the heat loss is calculated from:

$$Q_s = m^* \; Cp^* \; \Delta T \tag{61}$$

where:

Q_s = heat loss, watts

m^* = mols of outflow, $(\frac{3.91}{22.4})$mols/minute

Cp^* = heat capacity, (11.3 x 0.0698), watts/mol$^\circ$ C

ΔT = temperature difference, (550-20)$^\circ$C = 530° C

$$Q_s = \frac{(3.91)(11.3)(0.0698)(530)}{22.4} = 73 \text{ watts}$$

The heat conduction loss from the reactor was estimated from the following:

The reactor is a thin wall cylinder of stainless steel insulated with Johns-Manville cerafelt 400 five centimeters thick. The heat transfer is represented by:

$$Q_c = K_m \; A_m \; \frac{\Delta T}{x} \tag{62}$$

where:

Q_c = heat loss by conduction, watts

k_m = heat transfer coefficient, $(0.0221 \times 0.0698) \frac{\text{watts-cm}}{\text{cm}^2 \, ^\circ\text{C}}$

A_m = mean area, cm^2

Δt = temperature difference, $(550-20)^\circ\text{C} = 530^\circ\text{C}$

x = wall thickness, 5 cm

For short cylinders with uniform thickness of insulation McAdams (33) gives a plot of Am/A vs D/L from which A_m is estimated to be 885 square centimeters.

Therefore:

$$q = (0.0221)(0.0698)(885)(\frac{530}{5})$$

$$= 144 \text{ watts}$$

Heat into the reactor from the reactants is estimated as follows:

$$Q_{in} = Q_3 + Q_4 \tag{63}$$

$$= m_3 \, Cp_3 \; \Delta T + m_4 \; (Cp_4 \; \Delta T_1 \; + \tau) + m_4' Cp_4' \; \Delta T_2$$

Q_{in} = heat due to influx of reactants, watts

Q_3 = heat due to methane, watts

Q_4 = heat due to sulfur, watts

m_3 = mols methane, $\frac{1.3}{22.4}$ mols

m_4 = mols liquid sulfur, $\frac{5.2}{22.4}$ mols

m_4' = mols sulfur vapor, $\frac{2.6}{22.4}$ mols

Cp_3 = heat capacity methane, (16.0 x 0.0698) watts/^oC

Cp_4 = heat capacity sulfur liquid, (7.26 x 0.0698) watts/^oC

Cp_4' = heat capacity sulfur vapor, (9.0 x 0.0698) watts/^oC

τ = heat of vaporization sulfur, (2.15 x 69.8) cal/mol (34)

ΔT = temperature difference, (550-20)^oC = 530^o C

ΔT_1 = temperature difference, (444-20)^oC = 425^o C

ΔT_2 = temperature difference, (550-445)^oC = 115^o C

Substituting into equation (63) gives:

$$Q_{ra} = (\frac{1.3}{22.4})\ (16)\ (.0698)\ (530)$$

$$+ \frac{5.2}{22.4}\ (7.26)\ (.0698)\ (425) + (2.15)\ (69.8)$$

$$+ \frac{2.6}{22.4}\ (9.0)\ (.0698)\ (115) = 128 \text{ watts}$$

The total power required to sustain the reaction at constant temperature is calculated from equation (54)

$$Q_{req} = Q_{out} - Q_{in} = Q_r + Q_d + Q_s + Q_c - Q_{in}$$

$$= 32.2 + 190 + 73 + 144 - 128$$

$$= 311 \text{ watts}$$

Since the 311 watts of power necessary to sustain the reaction at required temperature is an estimate and also to give flexibility to the use of the proposed reactor by decreasing the time required to reach

steady state, a heater capable of 1500 watts power output is incorporated into the reactor vessel design. A variable transformer is used to control the power to the reactor heater according to the reaction temperature as indicated by a chromel-alumel thermocouple inside the reactor.

The power necessary to preheat the methane, to vaporize the sulfur and to preheat the sulfur vapor is estimated from equation (63) to be 35 watts for methane and 93 for the sulfur for a total of 128 watts. To provide an adequate amount of power for the preheaters and vaporizer the value of 128 was multiplied by a design factor of four to give a total of 511 watts.

Fisher and Smith (35) stated the primary problem in constructing and operating their tubular flow reactor was the corrosiveness of sulfur. They found that near 600° C the rate at which stainless steel is corroded is such that a reasonable long life can be expected for a reactor made of this material. Based on their experience the material specified for the reactor vessel, sulfur preheater, and outflow lines is type 316 stainless steel. The methane line, purifier and preheater will be made of glass or stainless steel while the sulfur vapor generator is to be constructed of glass and stainless steel. Chromel-alumel thermocouples are specified to measure the temperature of the inflowing reactants at the preheater exit and the reaction temperature in the reactor vessel. Detailed sketches of the reactor vessel and sulfur vapor generator are presented in Figures 4 and 5.

Extimates of the amount of reactants required for the reaction to reach steady state could be made since Denbigh (36) and Young (37) agreed that steady state would be reached with a maximum expenditure of reactant

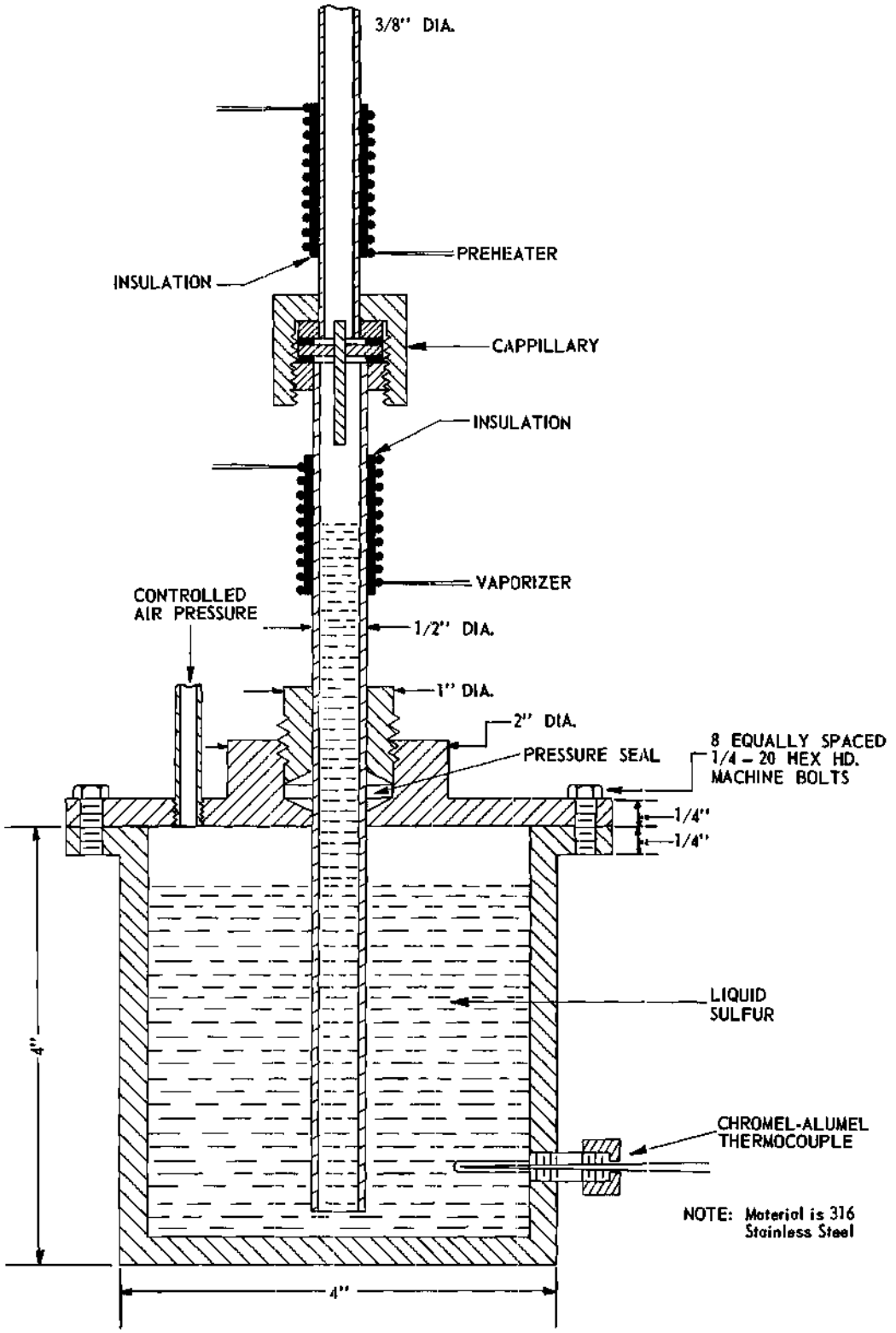

Figure 4. Sulfur Vapor Generator.

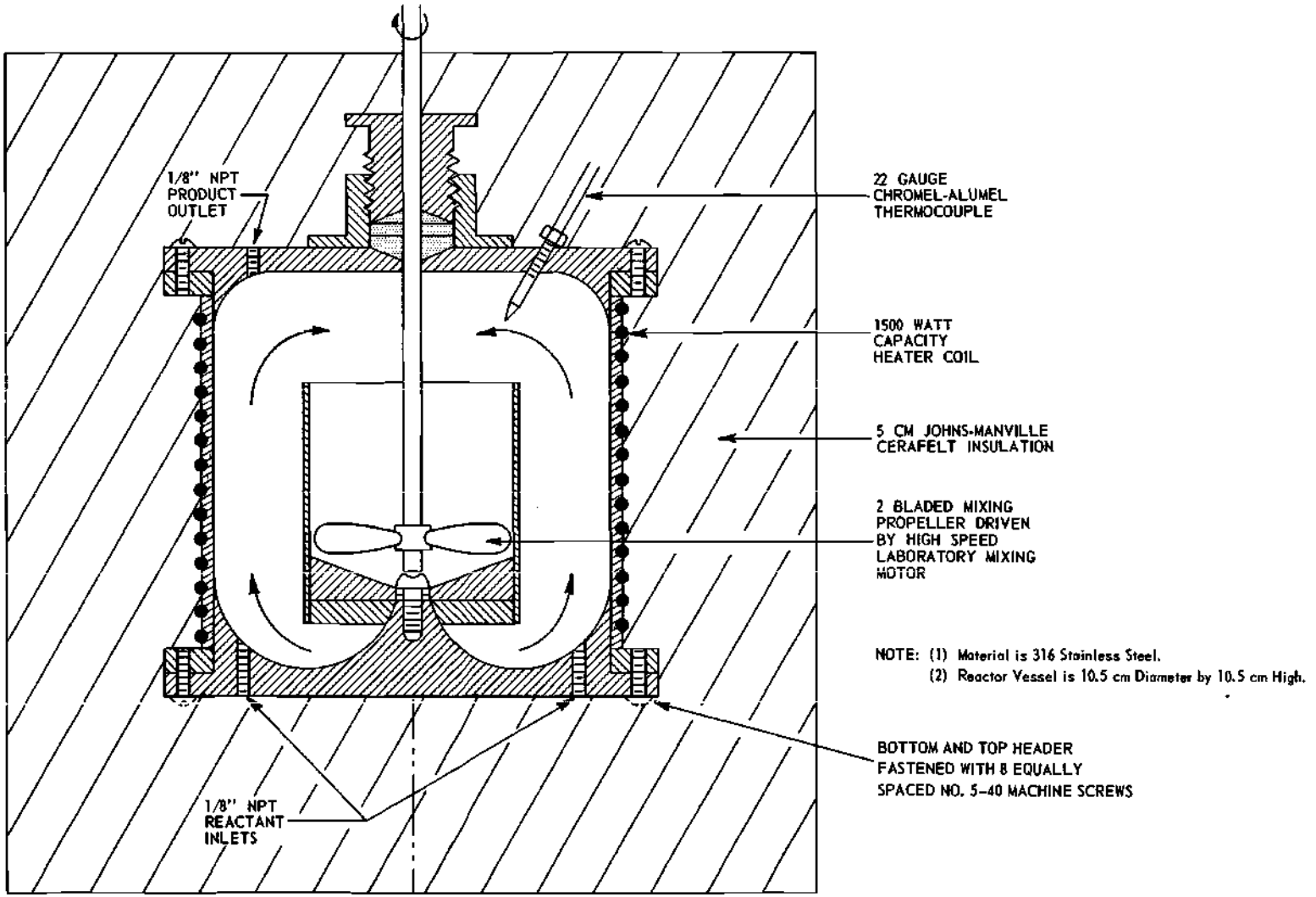

Figure 5. Reactor Vessel.

equal to eight times the volume of the reactor vessel regardless of the flow rate.

So:

$$V_T = (8)(V) \tag{64}$$

where:

V_T = maximum volume of reactants for steady state, liters

V = reactor volume, 1 liter

therefore:

$V = 8 \times 1 = 8$ liters

Then the volume of methane and sulfur which make up the total required to reach steady state are estimated:

$$V_1 = X_1 V_T \alpha \tag{65}$$

$$V_2 = X_2 V_T \alpha \tag{66}$$

where:

V_1 = volume of methane, standard liters

V_2 = volume of sulfur, standard liters

X_1 = fraction methane, 1/3

X_2 = fraction sulfur, 2/3

α = constant to convert to standard conditions from T = 550°C,

$$\frac{273}{823}$$

So:

$$V_1 = \frac{1}{3} (8) \frac{273}{823}$$

$$= 0.89 \text{ standard liters}$$

$$V_2 = \frac{2}{3}(8)\frac{273}{823}$$

$$= 1.78 \text{ standard liters}$$

To convert the volume of sulfur to weight of sulfur:

$$W_2 = V_2 \frac{1}{22.4} M_2 \tag{67}$$

where:

W_2 = weight sulfur, grams

V_2 = volume sulfur, 1.78 standard liters

M_2 = molecular weight sulfur; 64 gms/mol

so:

$$W_2 = 1.78 \frac{1}{22.4}(64) = 5.08 \text{ grams}$$

The minimum and maximum rate of product formation, as measured by rate at which CS_2 is formed, was estimated from the following analysis:

$$R_{1(max)} = X\, U_{max}\, Y \frac{1}{22.4} M_1 \tag{68}$$

where:

$R_{1(max)}$ = rate of CS_2 formation, gms/min

U_{max} = maximum volumetric flow rate, $(\frac{706.7}{60} \times \frac{273}{823})$ standard liters/min

X_1 = fraction of volume available for conversion to CS_2, 1/3

Y = fraction converted to CS_2, 0.2

M_1 = molecular weight CS_2, 76 gms/mol

Therefore:

$$R_{1(max)} = \frac{1}{3} \times \frac{706.7}{60} \times \frac{273}{823} \times 0.2 \times \frac{1}{22.4} \times 76$$

$$= 0.891 \text{ gms } CS_2 \text{ formed/min.}$$

The minimum rate of CS_2 formed was estimated from the same equation except that U_{min} = 0.157 liters per minute replaced U_{max} and Y = 0.4 was the conversion fraction. This gives:

$$R_{min} = \frac{1}{3} \times 0.157 \times 0.4 \times \frac{1}{22.4} \times 76$$

$$= 0.071 \text{ gms } CS_2 \text{ formed/min.}$$

The retention time is defined as the reactor volume divided by the volumetric flow rate. Therefore, the minimum retention time will be for the condition of maximum flow and the maximum retention time will be for the conditions of minimum flow. For the extreme flow conditions of this CFSTR system the maximum retention time is 6.5 minutes and minimum retention time is 0.085 minutes.

Since eight reactor volumes are the maximum required for the reaction to reach steady state, the maximum time required is eight times the retention time. The two extremes in this design are: 0.68 minutes and 52 minutes. These values are the maximum for the particular condition of the experiment and will be considerably smaller.

The important results from the design of the CFSTR system for the gas phase reaction between methane and sulfur are summarized as follows:

(1) Reactor volume - 1 liter

(2) Reactor configuration - Right cylinder, length equal diameter

(3) Reactor heater power capacity - 1500 watts

(4) Auxiliary power for preheaters and vaporizer - 511 watts

(5) Retention time - maximum: 6.5 minutes

minimum: .085 minutes

(6) Maximum time required to reach steady state

maximum: 52.0 minutes

minimum: 0.68 minutes

(7) Maximum reactant waste to reach steady state -

1.78 standard liters of methane

5.08 gms of sulfur

(8) Maximum rate of reactant consumption at steady state -

1.3 standard liters methane per minute

7.5 gms sulfur

(9) Rate of product formation - maximum: 0.89 gm/min.

minimum: 0.071 gm/min.

These results show that even for the most disadvantageous conditions the quantities of reactants are moderate, so that operating costs will be low. The rate of product formation should be adequate for easy analysis; however the length of time an experiment should run to give the optimum size product sample for analysis will have to be determined experimentally. From the drawings of the reactor vessel and the sulfur generator along with other design factor it is concluded that this design can be built for a relatively low cost because of its simplicity and small size.

Thus a design for a low constructing cost system, an inexpensive system with a low operating cost has been presented to determine the reaction rate constants for a homogeneous gas phase reaction.

It is noted that for this particular reaction the steady state is approached rapidly. For reaction with small rate constant this time might be extremely long and thereby limit the usefulness of the CFSTR system since the size and therefore the quantity of reactants would have to be increased proportionately.

Very high pressures pose the problems of the strength of the reactor, the measurement of flow rate and the rotary seals for the stirring equipment which limit the feasibility of CFSTR system under this condition.

CHAPTER IV

CONCLUSIONS

The following conclusions resulted from this study:

(1) Sufficient experimental work has been found in the literature to show that the CFSTR method can be used to determine accurately the rate constants of a wide variety of homogeneous liquid phase reactions.

(2) The determination of reaction rate constants for homogeneous gas phase reactions using a CFSTR is possible and in many cases advantageous.

(3) The use of the CFSTR method offers considerable mathematical simplification in the determination of rate constants of chemical reactions as compared with the two classical methods, the batch reactor method and the tubular flow method. This mathematical simplification is of particular importance in the determination of rate constants for complex or simultaneous reactions, since the integral equations that result from the analysis of these reactions by the tubular flow or batch methods, in most cases, can be solved only by tedious and lengthy approximation methods while the algebraic equations which come from the analysis of these reactions by the CFSTR method are no more difficult than the equations for simple reactions.

(4) The CFSTR method can be used to study reactions under constant conditions at any stage of the reaction since the rate of change of the concentration of all constituents is zero at steady state. This property makes the CFSTR method extremely important in the study of reaction which involve transient intermediate products.

(5) The CFSTR method requires a longer time for completion of an experiment than either the batch method or the continuous flow method for the same reaction. However, for many reactions the time necessary to complete an experiment can be made reasonable by properly designing the CFSTR system. For example, the system designed for the methane sulfur reaction would require approximately one hour to complete an experiment for the maximum conversion of 0.4 mol fraction of methane and approximately one and one half minutes to complete an experiment for the minimum conversion of 0.2 mol fraction of methane.

(6) The CFSTR method requires more chemicals than either the batch method or the tubular flow method because of the chemicals which flow to waste while the system is approaching steady state. However, it has been shown that the amount of chemicals necessary to reach steady state and to operate a CFSTR at steady state are not excessive for a properly designed system.

(7) A design of a CFSTR to determine the rate constants of the homogeneous gas phase reaction between methane and sulfur at atmospheric pressure is presented.

This design provides a simple low cost CFSTR system which can be used to determine the rate constants of gas phase reactions. In addition, the operating cost of this CFSTR system should be moderate since small quantities of chemical are required due to small volume (one liter) of the reactor vessel.

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